

# PATENT ABSTRACTS OF JAPAN

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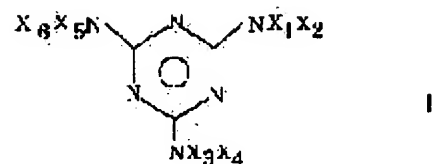
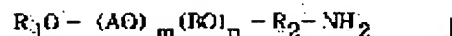
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## (54) CEMENT ADMIXTURE

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a cement admixture showing high flowability, having high flow survival rate and excellent in a day strength by including a formaldehyde addition condensation product of (A) a polyoxyalkylenemonoamine, (B) an alkoxyated product of melamine (or its derivative), (C) a compound capable of performing formaldehyde addition condensation with the ingredient B and (D) a sulfone group-forming compound as an essential ingredient.

SOLUTION: An ingredient A is expressed by formula I wherein R<sub>1</sub> is a 1-5C alkyl; R<sub>2</sub> is a 1-5C alkylene; AO and BO are each a 2-5C oxyalkylene and; (m) and (n) are each 0-300 and is e.g. polyoxyethylenemonoamine or the like. An ingredient B is expressed by formula II wherein X<sub>1</sub> to X<sub>6</sub> are each H, CH<sub>2</sub>OH or a 1-5C alkoxy. An ingredient C is e.g. melamine or its derivative. An ingredient D is sodium sulfite or the like. A molar ratio of (ingredient A: ingredient B: ingredient C) preferably is (0.005 to 0.5):(0.01 to 4):1. A molar ratio of (ingredient D: ingredients B and C) preferably is (1:0.3) to (1:4).



## LEGAL STATUS

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CLAIMS

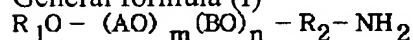
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## [Claim(s)]

[Claim 1] Cement admixture which uses as an indispensable component the formaldehyde addition condensation object of polyoxyalkylene monoamine (A), the alkoxy ghost (B) of the derivative and a melamine or the alkoxy ghost (B) of the derivative, the compound (C) in which formaldehyde addition condensation is possible, and the compound (D) which generates a sulfone radical. [ a melamine, ]

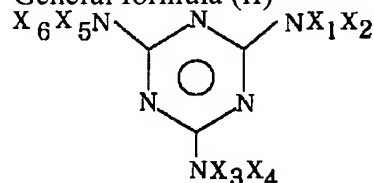
[Claim 2] Cement admixture according to claim 1 in which polyoxyalkylene monoamine (A) is shown by the following general formula (I).

General formula (I)



Here, the alkylene group AO of the alkyl group R<sub>2</sub>:carbon numbers 1-5 of the R<sub>1</sub>:carbon numbers 1-5 and the oxyalkylene radicals AO and BO of the BO:carbon numbers 2-5 are a block and/or Random m, and the integer of n:0-300. 300 >=m+n>=4 [ however, ] -- [Claim 3] Cement admixture according to claim 1 in which a melamine or the alkoxy ghost (B) of the derivative is shown by the following general formula (II).

General formula (II)

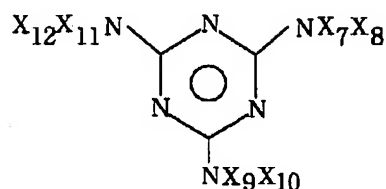


X<sub>1</sub>-X<sub>6</sub>: The inside of H, CH<sub>2</sub>OH, the alkoxy group of carbon numbers 1-5, however six substituents and at least one are the alkoxy group of carbon numbers 1-5, and [Claim 4] independently, respectively. Cement admixture according to claim 1 a melamine or the alkoxy ghost (B) of the derivative, and whose compounds (C) in which formaldehyde addition condensation is possible are a kind or two sorts or more of compounds chosen from the group of a melamine or its derivative, a phenol or its derivative, a urea or its derivative, aminobenzenesulfonic acid, its derivative, alkylamino benzenesulfonic acid, or its derivative.

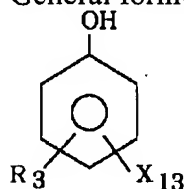
[Claim 5] Cement admixture according to claim 1 with which the compound (D) which generates a sulfone radical consists of a kind or two sorts or more of compounds chosen from the group which consists of a sodium sulfite, sodium bisulfite, a sodium pyrosulfite, an oleum, or a sulfur dioxide.

[Claim 6] Cement admixture according to claim 4 in which a melamine or its derivative is shown by the following general formula (III).

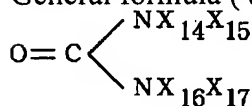
General formula (III)



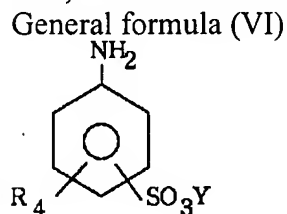
here -- X7-X12: -- Y:alkali metal independently chosen from H, CH<sub>2</sub>OH, or CH<sub>2</sub>SO<sub>3</sub>Y, respectively, alkaline earth metal, ammonium, an amine, and a permutation amine [claim 7] Cement admixture according to claim 4 in which a phenol or its derivative is shown by the following general formula (IV).  
General formula (IV)



here -- the alkyl group [claim 8] of X<sub>13</sub>:H, CH<sub>2</sub>OH or CH<sub>2</sub>SO<sub>3</sub>Y, sulfone radical or its alkali-metal salt, alkaline-earth-metal salt, ammonium salt, amine, permutation amine Y:alkali-metal, alkaline-earth-metal, ammonium, amine, and permutation amine R<sub>3</sub>:H or carbon numbers 1-6 Cement admixture according to claim 4 in which a urea or its derivative is shown by the following general formula (V).  
General formula (V)



here -- X<sub>14</sub>-X<sub>17</sub>: -- Y:alkali metal independently chosen from H, CH<sub>2</sub>OH, or CH<sub>2</sub>SO<sub>3</sub>Y, respectively, alkaline earth metal, ammonium, an amine, and a permutation amine [claim 9] Cement admixture according to claim 4 in which aminobenzene sulfonic acid, its derivative, alkylamino benzenesulfonic acid, or its derivative is shown by the following general formula (VI).



Here, it is the alkyl group of Y:H, alkali-metal, alkaline-earth-metal, ammonium, amine, and permutation amine R<sub>4</sub>:H or carbon numbers 1-6.

[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the admixture of cement or a cement constituent, in detail, in case hydraulic cement constituents, such as cement paste, mortar, and concrete, are kneaded, it adds, and this invention relates to the admixture for cement which improves the workability.

[0002]

[Description of the Prior Art] Conventionally, cement admixture is used from a viewpoint which improves many engine performance, such as reinforcement of cement hardened materials, such as mortar and concrete, and endurance or crack prevention. As typical admixture, what uses the salt of beta-naphthalene sulfonic-acid formaldehyde quantity condensate, the salt of a melamine sulfonic-acid formaldehyde condensate, a ligninsulfonic acid salt, an amino sulfonic acid condensate, hydroxy acid, etc. as a principal component is known.

[0003] If such admixture is added in the kneading object which consists of cement, water, and the aggregate, since kneading will become possible at low water and a cement ratio, it is useful to improvement of hydraulic cement constituents, such as cement paste, mortar, and concrete, on the strength. However, development of admixture with which the further high-intensity-izing of precast concrete or the structure and high fluidization are desired, and good workability is acquired by still lower water and the cement ratio is desired in recent years.

[0004] So, admixture various in the past is developed. For example, the copolymerization objects (JP,3-285856,A, JP,4-74748,A, etc.) of the olefin of carbon numbers 2-8 and an ethylene nature partial saturation dicarboxylic acid anhydride are known. Have a still higher dispersion effect according to the steric hindrance of the side chain of the hydrophilic property which furthermore projected from the principal chain. copolymerization objects (JP,59-18338,B --) with the polyalkylene glycol monoester system monomer, acrylic-acid (meta) system monomer, and/or partial saturation dicarboxylic acid system monomer which have an unsaturated bond JP,2-7897,B, JP,2-7898,B, JP,2-7901,B, Water-soluble vinyl copolymers (these are named generically and it is described as a polycarboxylic acid system below), such as JP,2-8983,B, JP,2-11542,B, JP,5-11057,B, and JP,6-88817,B, are mentioned. Furthermore, the condensation product (JP,6-340459,A) which introduced the polyalkylene glycol chain into the aromatic compound is also developed recently.

[0005] However, while these compounds show the outstanding convection effect, they have various kinds of troubles. First, the water reducing agent of a polycarboxylic acid system has a carboxyl group in intramolecular. This carboxyl group has large bonding strength with calcium ion. So, these compounds catch the calcium ion in cement, and when there are many additions, coagulation delay becomes large, and they have the trouble that it cannot shift to the next activity.

[0006] Furthermore, the polycarboxylic acid system which has an oxyalkylene chain in intramolecular has large air taking nature, and it is difficult for it to adjust the air content in concrete. Although the air content is actually controlled using a defoaming agent, there is a trouble of changing an air content sharply and being hard to use it by the agitator conditions and conveyance time amount of the kneading

conditions in a concrete mixer or a concrete mixer truck. Moreover, when used as an object for concrete secondary products, for the taken air, an opening occurs on a front face and there is a fault that front-face nature is inferior. Furthermore, since it copolymerizes using an acrylic-acid (meta) system monomer and/or a partial saturation dicarboxylic acid system monomer, although it has a carboxyl group in the intramolecular in these compounds, the trouble that hardening delay becomes large is in a sake by the presentation ratio. That is, the early age strength of cement mortar or concrete falls. Furthermore, in using large namely, the soft mortar or the concrete of a slump, segregation may be caused and it has been a problem. Moreover, there is a trouble that the convection effect of the polycarboxylic acid system average which has an oxyalkylene chain in intramolecular is not accepted about the condensation product which introduced the polyalkylene glycol chain into the aromatic compound.

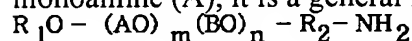
[0007]

[Means for Solving the Problem] this invention persons found out having the outstanding dispersion effect and remarkable segregation resistance, without a compound with a certain specific molecular structure causing hardening delay, as a result of inquiring wholeheartedly in order to solve these troubles. Moreover, the front-face nature of the precast concrete which added and fabricated this compound found out excelling remarkably. Furthermore, when this compound is back-\*(ed) like a plasticizer, it came to make header this invention for the especially excellent convection effect being shown.

[0008] That is, it is related with the cement admixture which uses as an indispensable component the formaldehyde addition condensation object of polyoxyalkylene monoamine (A), a melamine, the alkoxy ghost (B) of the derivative and a melamine or the alkoxy ghost (B) of the derivative, the compound (C) in which formaldehyde addition condensation is possible, and the compound (D) which generates a sulfone radical.

[0009]

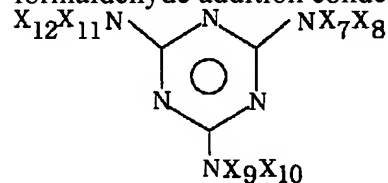
[Embodiment of the Invention] Below, this invention is explained at a detail. As polyoxyalkylene monoamine (A), it is a general formula (I).



Here, the alkylene group AO of the alkyl group R2:carbon numbers 1-5 of the R1:carbon numbers 1-5 and the oxyalkylene radicals AO and BO of the BO:carbon numbers 2-5 are a block and/or Random m, and the integer of n:0-300. However, they are polyoxyalkylene monoamines, such as the compound shown by  $300 \geq m+n \geq 4$ , i.e., polyoxyethylene monoamine, polyoxypropylene monoamine, and polyoxyethylene oxypropylene monoamine. This oxyalkylene part has desirable carbon numbers 2-5.

[0010] Although \*\*\*\*\* [ the number of oxyalkylene / one ], a block or the thing combined at random is sufficient as two or more kinds of oxyalkylene. As a repeat unit, it is 4-300 pieces preferably, and they are 7-100 pieces still more preferably. It can obtain easily by methylol-izing a melamine or its derivative with formaldehyde, and making it react with alcohol, such as a methanol, further as a melamine or an alkoxy ghost (B) of the derivative.

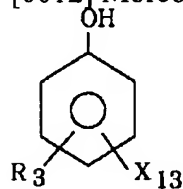
[0011] As the alkoxy ghost (B) of a melamine or its derivative, and a compound (C) in which formaldehyde addition condensation is possible, it is a general formula (III).



here -- X7-X12: -- the compound shown by Y:alkali metal independently chosen from H, CH<sub>2</sub>OH, or CH<sub>2</sub>SO<sub>3</sub>Y, respectively, alkaline earth metal, ammonium, the amine, and the permutation amine, i.e., a melamine, a methylol radical content melamine, a sulfo methyl group content melamine, etc. can be used. In the case of a sulfo methyl group content melamine, the salts can also be used. As salts, alkali-

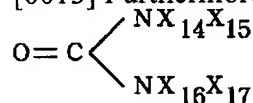
metal salts, such as mineral, i.e., a potassium, sodium, and magnesium, alkaline-earth-metal salts or organic salt, i.e., ammonium salt, a monoethanolamine salt, a diethanolamine salt, etc. can be used.

[0012] Moreover, it is a general formula (IV) as others.



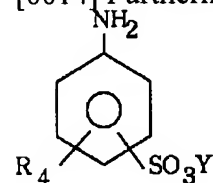
Here X13: H, CH<sub>2</sub>OH or CH<sub>2</sub>SO<sub>3</sub>Y, a sulfone radical, or its alkali-metal salt, An alkaline-earth-metal salt, ammonium salt, an amine, the permutation amine Y : Alkali metal, The compound shown by the alkyl group of alkaline-earth-metal, ammonium, amine, and permutation amine R3: H or carbon numbers 1-6, Namely, alkylphenols, such as a phenol, cresol, p-t-butylphenol, and p-t-p tert amylphenol, or the sulfonic acids or the salt of a sulfonic acid Or a methylol radical content phenol, sulfo methyl group content phenols, or those salts can be used. As salts, the mineral and organic salt as well as a general formula (III) can also be used. Especially, a phenol, a methylol radical content phenol, a sulfo methyl group content phenol or phenolsulfonic acid, and its salts are economically desirable also from reactivity.

[0013] Furthermore, a general formula (V)



here -- X14-X17: -- the compound shown by Y:alkali metal independently chosen from H, CH<sub>2</sub>OH, or CH<sub>2</sub>SO<sub>3</sub>Y, respectively, alkaline earth metal, ammonium, the amine, and the permutation amine, i.e., a urea, a methylol radical content urea, and a sulfo methyl group content urea can also be used. In the case of a sulfo methyl group content urea, the mineral and organic salt as well as a general formula (III) can also be used.

[0014] Furthermore, a general formula (VI)



Here, aminobenzene sulfonic acid, such as an alkyl group of Y: H, alkali-metal, alkaline-earth-metal, ammonium, amine, and permutation amine R4: H or carbon numbers 1-6, i.e., a sulfanilic acid, methanic acid, and an ORUTANIN acid, or the salts of those can be used. As salts, the mineral and organic salt can be used like a general formula (III). Especially, a sulfanilic acid, methanic acid, and its salts are economically desirable also from reactivity.

[0015] As a compound (D) which generates a sulfone radical, well-known sulfonation agents, such as a sodium sulfite, sodium bisulfite, a sodium pyrosulfite, a sulfur dioxide, and an oleum, can be used.

[0016] For example, the approach of introducing a sulfo methyl group into the melamine of a general formula (III) can be performed by the well-known approach. That is, after carrying out addition condensation of the formaldehyde to a melamine and considering as a methylol melamine, it is possible to introduce by making a sulfonation agent act and changing for a hydroxyl group. It is known that six-mol formaldehyde will carry out addition condensation to one mol of melamines as a methylol radical. In this invention, since possibility that the methylol radical for two mols will be used for addition copolycondensation is high, installation of a sulfo methyl group is possible for max on the remaining methylol radicals for four mols. When an economical field and the convection effect of a reactant acquired are taken into consideration, the amount of installation of a sulfo methyl group has desirable

0.3-4 mols, and its installation it is [ installation ] 0.5-2 mols is more desirable.

[0017] It is also the same as when introducing a sulfo methyl group into the phenol of a general formula (IV), and 0.5-1.5 mols are [ the amount of installation of 0.3-2 mols per one mol of phenols is desirable still more desirable, and ] suitable. It is also the same as when introducing a sulfo methyl group into the urea of a general formula (V), and 0.5-1.5 mols are [ the amount of installation of 0.3-2 mols per one mol of ureas is desirable still more desirable, and ] suitable.

[0018] The formaldehyde which is used in compounding these formaldehyde addition condensation objects can usually be used by the thing of 30 - 60% of the weight of concentration. Furthermore, it is also possible to use a paraformaldehyde together if needed. 1 - 6 time mol of the total number of mols of the compound (C) in which the melamine, the alkoxy ghost (B) of that derivative and the melamine or the alkoxy ghost (B) of that derivative, and formaldehyde addition condensation of the amount of this formaldehyde used are possible -- using is desirable. When economical efficiency, the ease of a condensation reaction, etc. are taken into consideration, it is more desirable to use a mol 1.5 to 4 times.

[0019] A formaldehyde addition condensation reaction is performed by the usual approach of the range of pH 4-12, and the so-called weak acidic field to a basic field. Since it becomes difficult to control a reaction -- a condensation reaction advances rapidly and may gel -- by less than four pH, it is not desirable. Moreover, addition of formaldehyde may be beforehand taught in a reactor, and formalin may be dropped and it may make it react in the middle of a reaction.

[0020] The presentation of the compound which constitutes the admixture in this invention is important. Namely, a polyoxyalkylene (monoamine A):melamine or the alkoxy ghost of the derivative (B): It is desirable still more desirable that it is  $:(0.005-0.5) (0.01-4):1$ , and  $:(0.01-0.35) (0.1-1):1$  is suitable for the mole fraction of the alkoxy ghost (B) of a melamine or its derivative, and the compound (C) in which formaldehyde addition condensation is possible. It is desirable still more desirable that it is  $1:0.3-1:4$ , and  $1:0.5-1:2$  are suitable for the mole fraction of compound (D): [the compound (C) in which a melamine or the alkoxy (ghost B) + formaldehyde addition condensation of the derivative is possible] which generates a sulfone radical.

[0021] Next, although the example of the concrete manufacture approach of the cement admixture in this invention is shown below, this invention is not limited to this.

After teaching example 1 melamine or the alkoxy ghost (B) of the derivative, a melamine or the alkoxy ghost (B) of the derivative and the compound (C) in which formaldehyde addition condensation is possible, formaldehyde, and water to 4 opening flask which an agitator, a thermometer, reflux tubing, and a tap funnel attached and carrying out the temperature up of the reactor internal temperature to 60-90 degrees C, it is made to react under basicity for 0.5 to 2 hours. Next, the compound (D) which generates a sulfone radical is added and it is made to react at 60-90 degrees C for 0.5 to 3 hours. After adding polyoxyalkylene monoamine (A) furthermore and making the inside of a system into the acescence, it is made to react at 50-80 degrees C. If the viscosity of a solution reaches a predetermined value, it will neutralize and a reaction will be stopped. Although the predetermined viscosity which stops a reaction changes with nonvolatile matters of a solution, when a nonvolatile matter is 35 % of the weight, 7 - 500cp / 25 degrees C have the desirable measured value in a Brookfield viscometer, and its 10 - 300cp / 25 degrees C are still more desirable.

[0022] After teaching polyoxyalkylene monoamine (A), a melamine, the alkoxy ghost (B) of the derivative and a melamine or the alkoxy ghost (B) of the derivative, the compound (D) that generates the compound (C) in which formaldehyde addition condensation is possible, formaldehyde, and a sulfone radical, and water to 4 opening flask which example 2 agitator, a thermometer, reflux tubing, and a tap funnel attached, it is made to react to it at 70-90 degrees C for 0.5 to 8 hours. Next, the inside of a system is made into the acescence and it is made to react at 50-80 degrees C. If the viscosity of a solution reaches a predetermined value, it will neutralize and a reaction will be stopped. The predetermined viscosity which stops a reaction is the same as that of an example 1.

[0023] Concomitant use with other water reducing agents known from the former, an AE water-reducing agent, a high-range water reducing agent, a high-performance AE water-reducing agent, and a plasticizer is also possible for the cement admixture of this invention. That is, it can use together with the salt of



beta-naphthalene sulfonic-acid formaldehyde quantity condensate, the salt of a melamine sulfonic-acid formaldehyde condensate, the salt of an aminosulfonic acid condensate, a ligninsulfonic acid salt, hydroxy acid, a polycarboxylic acid system water reducing agent, an alkali hydrolysis mold water reducing agent, a gradual release mold high-range water reducing agent, etc.

[0024] Concomitant use with well-known cement admixture, for example, an air entraining agent, a defoaming agent, a setting accelerator, retarding admixture, a rust-proofer, antiseptics, a waterproofing agent, an accelerator on the strength, etc. is also possible, concerning the operation of the cement admixture of this invention. Moreover, although the operation is usually mixed to kneading underwater and it adds to a cement constituent, any are sufficient as the approach of adding at once at the time of preparation of a cement constituent or the approach of dividing and adding, the approach of carrying out adding after mixing to the cement constituent after \*\*\*\*\*, etc. Although the addition of the cement admixture concerning this invention changes with applications of combination or a cement constituent, to cement, it is solid content conversion and is usually preferably used at 0.05 - 3.0% of the weight of a rate 0.01 to 5.0% of the weight. At less than 0.01 % of the weight, since a distributed fluidity falls, the amount used is not desirable. Moreover, it becomes economically or disadvantageous and is not desirable if 5.0 % of the weight is exceeded.

[0025] The cement admixture concerning this invention is applicable to the concrete and mortar which are prepared using various Portland cement, fly ash cement, Portland blast furnace cement, pozzolanic cement, various blended cement, etc. Furthermore, it is applicable also to the concrete which blended silica fume, a blast furnace slag, limestone impalpable powder, etc. Although the reason which shows the convection effect in which the cement admixture of this invention was excellent, without showing coagulation delay, and segregation resistance is not in \*\*, it is guessed as follows.

[0026] By the anion radical in a molecule, cement admixture sticks to a cement front face, and makes the surface charge negative. It is thought that electric repulsive force distributes the cement particle charged in negative. However, when the cement admixture molecule itself has a charge too much, it is difficult for cement admixture to oppose with the charge and to form a many layers admixture layer on a cement particle front face. When nonionic structure exists moderately in a cement admixture molecule, through a nonionic part, admixture sticks to many layers on a cement particle front face, and they enlarge the density of electric charge of a cement particle.

[0027] This invention introduces nonionic structure into intramolecular by making a melamine or the alkoxy ghost (B) of the derivative introduce into the molecule which constitutes cement admixture. Consequently, the adsorption thickness of the cement admixture molecule to a cement particle front face increases, and it is surmised that a high dispersion effect is acquired. Moreover, when the cement admixture of this invention sticks to a cement particle, the polyoxyalkylene group which it has in intramolecular is considered to be extended on the outside of a cement particle. A hydration sphere is formed in the surroundings of the polyoxyalkylene group extended on this outside, he carries out long duration maintenance of the dispersibility of a cement particle according to the steric hindrance effectiveness accompanying this, and it is thought that slump loss is controlled.

[0028] Furthermore, like the conventional gradual release mold high-range water reducing agent, a polycarboxylic acid system water reducing agent, and an alkali hydrolysis mold water reducing agent, since it does not have the high carboxyl group of calcium ion and chelate ability in intramolecular, it is expected that coagulation retardancy is not shown. So, the cement admixture of this invention has the outstanding dispersibility ability and high segregation resistance.

[0029] Moreover, the reason the cement admixture of this invention shows the convection effect which was excellent especially at the time of adding after mixing is guessed as follows. Cement admixture is divided into a sulfone radical system and a carboxy group system by the class of the anion radical. When it adds at the beginning of kneading of the admixture of a sulfone radical system of a cement constituent, since polarization of intramolecular is large compared with a carboxyl group, it sticks to a sulfone radical quickly by the aluminates layer just charged on the cement particle front face. After contacting water, in order that this aluminates layer may form hydrates, such as ettringite, in an instant, the cement admixture to which it stuck is incorporated by this, and loses effectiveness. However, when cement

admixture is added after it contacted water beforehand and the hydration of an aluminates layer advanced like a plasticizer, it sticks to the added cement admixture in the silicate layer considered to be effective in a convection effect, without being incorporated by the hydrate. Although the admixture shown in this invention is the admixture of a sulfone radical system, even if it makes late the rate of adsorption to an aluminates layer and is added by introducing nonionic structure into intramolecular at the beginning of kneading, a high convection effect is acquired. However, when it adds after hydrates, such as ettringite, formed, as shown above, all stick to a silicate layer and it is thought that the further excellent convection effect discovers the front face since it is strongly charged by the sulfone radical. [0030] Although the following examples explain the cement admixture of this invention in more detail, this invention is not limited to this. Moreover, especially % or the section indicated as a numerical unit below will be weight % or the weight section altogether, if unstated. Moreover, the polyoxyalkylene monoamine (A) used for the example is JEFFAMINE of San Techno Chemical. M series was used. Each physical-properties value is indicated to Table 1.

[0031]

[Table 1]

名称	PO/EO # 1	平均分子量 # 2
JEFFAMINE M - 1000	3/19	1000
JEFFAMINE M - 2070	10/32	2000

#1 Mole-fraction #2 of the propylene oxide contained in a molecule with PO/EO, and ethyleneoxide Although the melamine which shows molecular weight by the weight-average-molecular-weight general formula (II), or the alkoxy ghost (B) of the derivative was easily obtained by carrying out alkoxy \*\* of the methylol ghost of a melamine in various alcohol, in this invention, the commercial item shown in Table 2 was used for it.

[0032]

[Table 2]

名称	平均分子量
サイメル350	185
サイメル385	205

[0033] Example of example manufacture 1 Cymel 350 0.10 mols (18.5 sections), 0.50 mols (63.1 sections) of melamines, 0.12 mols (11.3 sections) of phenols, 0.2 mols (12.0 sections) of ureas, After teaching 4 opening flask with which an agitator, a thermometer, reflux tubing, and a tap funnel attached the 0.18 mol [ of sulfanilic acids ] (31.2 sections), 3.0 mol [ of 37% formalin ] (243.2 sections), and water 320.0 section and carrying out the temperature up of the reactor internal temperature to 70 degrees C, it was made to react under basicity for 1 hour. Furthermore 0.55 mols (57.3 sections) of sodium bisulfite were added, and it was made to react at 80 degrees C for 1.5 hours. The water 123.0 section was added and it cooled to 60 degrees C. Then, M-1000 After supplying 0.04 mols (40.0 sections), pH in a system was set to 6.0 with the sulfuric acid 40%. When carry out a temperature up to 65 degrees C, it was made to react and the viscosity of a solution became 21cp / 25 degrees C, the sodium-hydroxide water solution neutralized 25%, and the reaction was stopped. The obtained product was made into the reactant 1.

[0034] In 4 opening flask which example of manufacture 2 agitator, a thermometer, reflux tubing, and a tap funnel attached Cymel 350 0.20 mols (37.0 sections), 1.0 mols (126.1 sections) of melamines, 1.0 mols (104.1 sections) of sodium bisulfite, M-2070 The 0.15-mol (300.0 sections), 3.0 mol [ of 37% formalin ] (243.2 sections), and water 1025.0 weight section was set into \*\*\*\*, pH was set to 11.5 for the inside of a system by the sodium hydroxide 25%, and it was made to react at 80 degrees C for 4

hours. Next, after cooling the inside of a system to 60 degrees C and making it pH6.0 with a sulfuric acid 40%, when the viscosity of a solution became 28cp / 25 degrees C, the sodium-hydroxide water solution neutralized 25%, and the reaction was stopped. The obtained product was made into the reactant 2.

[0035] By the same approach as the example 3 of manufacture - the example 1 of 4 manufactures, as shown in Table 3, the presentation of a compound and viscosity were changed and compounded. Consequently, reactants 3-4 were obtained.

[0036] By the same approach as the example 5 of manufacture - the example 2 of 6 manufactures, as shown in Table 3, the presentation of a compound and viscosity were changed and compounded. Consequently, reactants 5-6 were obtained.

[0037] Except having not used the polyoxyalkylene monoamine (A) shown by example of manufacture 7 general formula (I), it is the same approach as the example 1 of manufacture, and as shown in Table 3, the presentation of a compound was changed and compounded. Consequently, the reactant 7 was obtained.

[0038] Except having not used the melamine shown by example of manufacture 8 general formula (I), or the alkoxy ghost (B) of the derivative, it is the same approach as the example 1 of manufacture, and as shown in Table 3, the presentation of a compound was changed and compounded. Consequently, the reactant 8 was obtained.

[0039] Except having not used example of manufacture 9 melamine or the alkoxy ghost (B) of the derivative, and the compound (C) in which formaldehyde addition condensation is possible, it is the same approach as the example 1 of manufacture, and as shown in Table 3, the presentation of a compound was changed and compounded. Consequently, the reactant 9 was obtained.

[0040] Except having not used the compound (D) which generates an example of manufacture 10 sulfone radical, it is the same approach as the example 1 of manufacture, and as shown in Table 3, the presentation of a compound was changed and compounded. Consequently, the reactant 10 was obtained.

[0041] Except having not used example of manufacture 11 formaldehyde, it is the same approach as the example 1 of manufacture, and as shown in Table 3, the presentation of a compound was changed and compounded. Consequently, the reactant 11 was obtained.

[0042] Using the compulsive biaxial mold concrete mixer of 150l. of examples, based on the combination for a concrete trial shown in Table 4, 40l. the reactant 1 and water which were obtained by cement, coarse aggregate, and the example 1 of manufacture so that it might scour and might become the amount of risers were thrown in, \*\*\*\*\* was performed for 90 seconds, coarse aggregate was thrown in further, and it kneaded for 3 minutes. The hi-performance concrete of 60\*\*2cm of slump flows and 3\*\*1% of air contents was prepared. In order to make it a target air content, when entrained airs ran short, air entraining agent Vaughan Sol by Yamaso Chemical [ CO., LTD. ] CO., LTD. was used, and when an air content entered too much, it adjusted using Di Luc Wright 850 by the Hok Cong Industrial company as a defoaming agent. It scoured and aging of a slump and a slump flow was measured until after 90 minutes every 30 minutes after going up. Moreover, compressive strength produced the cylinder mold specimen with a phi10cmx height of 20cm, and measured it in one day, seven days, and 28 days. Moreover, about segregation resistance, at the time of slump flow measurement, the degree of migration of the aggregate was observed visually and relative evaluation of O, O, \*\*, and x was performed. In addition, the production approach of the specimen for compressive strength was altogether performed in a slump, an air content, the setting time and the measuring method of compressive strength, and the list based on Japanese Industrial Standards (JIS-A6204). A result is shown in Table 5.

[0043]

[Table 3]

製造例 No		1	2	3	4	5	6	7	8	9	10	11
反応物 No		1	2	3	4	5	6	7	8	9	10	11
A	M-1000	0.04		0.5		0.3	0.1		0.04	0.04	0.04	0.04
	M-2070		0.15		0.01		0.01					
B	サイメル 350	0.10	0.20	0.40		0.30	0.20	0.10		0.10	0.10	0.10
	サイメル 385				0.20							
C	メラミン	0.50	1.00	0.80	0.70	0.90	0.75	0.50	0.50		0.50	0.50
	スルフォメ チル化メラ						0.25					
	フェノール	0.12		0.15				0.12	0.12		0.12	0.12
	尿素	0.20			0.10			0.20	0.20		0.20	0.20
	スルフォメ チル化尿素			0.05								
	スルファニ ル酸	0.18			0.20			0.18	0.18		0.18	0.18
	メタニル酸					0.10						
	B群 Total	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0	1.00	1.00
D	重亜硫酸 ナトリウム	0.55	1.00	4.20		0.50	0.40	0.55	0.55	0.55		0.55
	亜硫酸 ナトリウム			0.30		0.50						
	ピロ亜硫酸 ナトリウム				0.50							
E	ホルム アルデヒド	3.00	3.00	7.00	3.40	3.20	2.50	3.20	3.20	3.20	3.20	
樹脂濃度 (%)		35	35	35	35	35	35	35	35	35	35	6
粘度 (cps/25℃)		22	23	16	24	24	20	15	16	7	204	6

[0044]

[Table 4] Combination for a concrete trial

W/C (%)	s/a (%)	単位量 (kg/m <sup>3</sup> )				目標空気量 (%)
		C	W	S	G	
33	40	533	176	643	1013	3±1

[0045] W/C: Water/cement (% of the weight)

s/a: Fine aggregate/(fine aggregate + coarse aggregate) (capacity %)

C: charge cement of cement S: fine aggregate G: coarse aggregate concrete kneading material: -- three-sort mixing ordinary portland cement (MITSUBISHI MATERIALS CORP. --) Chichibu Onoda Cement, Inc. Tokuyama specific gravity =3.16 fine-aggregate: -- weathered granite system natural sand from Hiroshima Kamo Nyuno, Kochi-cho specific gravity =2.57 coarse-aggregate: -- 5,  
 \*\*\*\*\* , Ishihara, Shimonoseki-shi, Yamaguchi-ken: -- crushed stone 6 No. =1:1  
 charge cement of specific gravity =2.69 concrete kneading material: -- three-sort mixing ordinary portland cement MITSUBISHI MATERIALS CORP. and Chichibu Onoda Cement, Inc. -- Tokuyama specific gravity =3.16 fine-aggregate: -- weathered granite system natural sand from Hiroshima Kamo

Nyuno, Kochi-cho specific gravity =2.57 coarse-aggregate: -- 5, \*\*\*\*\*, Ishihara, Shimonoseki-shi, Yamaguchi-ken: -- crushed stone 6 No. =1:1 specific-gravity = -- 2.69 [0046] The same actuation as an example 1 was performed except having used two to example 6 reactants 2-6. A result is shown in Table 5.

[0047] The same actuation as an example 1 was performed except having used one to example of comparison 5 reactants 7-11. A result is shown in Table 5.

[0048] The mel flow 40 (Mitsui Chemicals, Inc.: melamine system) which is a commercial high-range water reducing agent as a water reducing agent the example 6 of a comparison - for 10 comparison contrast, My tea 150 (Kao Corp.: naphthalene system), PARIKKUFP200U (Fujisawa Pharmaceutical Co., Ltd.: aminosulfonic acid system), The same actuation as an example 1 was performed using my tea 2000WH (Kao Corp.: naphthalene system + activity self-sustaining matter) of the gradual release mold which is a high-performance AE water-reducing agent, and CHU pole HP-8 (Takemoto Fats and oils: polycarboxylic acid system). A result is shown in Table 5.

[0049]

[Table 5]

	セメント混和剤	添加量 (%)	スランプ (cm)				フロー残存率 (%)	圧縮強度 (MPa)			材料分離抵抗性
			0分	30分	60分	90分		1日	7日	28日	
実施例 1	反応物 1	0.35	61	55	55	51	83.6	21.0	55.8	64.6	◎
実施例 2	反応物 2	0.32	60	58	56	46	76.7	19.9	54.0	63.0	○
実施例 3	反応物 3	0.36	61	56	54	50	82.0	21.0	55.4	64.3	◎
実施例 4	反応物 4	0.39	60	56	51	46	76.7	20.3	54.0	65.0	◎
実施例 5	反応物 5	0.31	62	56	50	49	79.0	20.2	54.1	64.1	◎
実施例 6	反応物 6	0.38	61	57	51	50	82.0	20.0	56.4	63.8	◎
比較例 1	反応物 7	1.00	60	50	42	38	63.3	19.8	52.6	63.8	○
比較例 2	反応物 8	0.42	60	55	52	49	81.7	17.9	53.1	64.3	○
比較例 3	反応物 9	3.00	直立	直立	直立	直立	—	—	—	—	—
比較例 4	反応物 10	3.00	直立	直立	直立	直立	—	—	—	—	—
比較例 5	反応物 11	3.00	直立	直立	直立	直立	—	—	—	—	—
比較例 6	メルフロー 40	1.00	59	49	43	35	59.3	19.3	53.1	64.5	○
比較例 7	マイティー 150	1.05	60	48	42	34	56.7	16.7	53.1	63.2	△
比較例 8	バリック FP200U	0.65	60	52	45	39	65.0	16.9	53.7	62.5	△
比較例 9	マイティー 2000WH	0.70	59	53	47	42	71.2	16.3	52.9	61.9	△
比較例 10	チューボール HP-8	0.50	61	55	50	41	67.2	17.2	54.6	64.3	△

[0050] Back \*\*\*\*\* is compared with the 7th example. The high-range water reducing agent mel flow 40 was used, and the base concrete of 50\*\*2cm of slump flows and 3\*\*1% of air contents was adjusted. Adjustment of the kneading approach and an air content was performed by the same approach as an example 1. The reactant obtained in the example 1 of manufacture was supplied to this scoured base concrete, and the concrete of 60\*\*2cm of slump flows and 3\*\*1% of air contents was adjusted by the same approach as an example 1. Aging of a slump was measured until after 90 minutes every 45 minutes after that. Moreover, about the air content, adjustment by the defoaming agent and the air entraining agent was not carried out, but immediately after the second kneading was measured. About compressive strength and segregation resistance, it carried out by the same approach as an example 1. A result is shown in Table 6.

[0051] It carried out like the example 1 except having used eight to example 13 reactants 2-6. A result is

shown in Table 6.

[0052] It carried out like the example 1 except having used 11 to example of comparison 15 reactants 7-11. A result is shown in Table 6.

[0053] The same actuation as an example 1 was performed using CHU pole HP-8 (Takemoto Fats and oils: polycarboxylic acid system) which is the mel flow 40 (Mitsui Chemicals, Inc.: melamine system) which is a commercial high-range water reducing agent, my tea 150 (Kao Corp.: naphthalene system), and a high-performance AE water-reducing agent as a water reducing agent the example 16 of a comparison - for 18 comparison contrast. A result is shown in Table 6.

[0054]

[Table 6]

	セメント 混和剤	添加量 (%)	スランプ (cm)				スラン プ残存 率 (%)	空気量 (%)		圧縮強度 (MPa)			材料分離 抵抗性
			添加前	添加後	45分	90分		添加前	添加後	1日	7日	28日	
実施例 7	反応物 1	0.15	50.0	60.0	57.0	49.0	81.7	3.0	3.1	20.0	58.1	65.3	◎
実施例 8	反応物 2	0.13	51.0	61.0	58.0	48.0	78.7	3.0	3.0	20.4	55.0	64.3	◎
実施例 9	反応物 3	0.14	52.0	60.0	55.0	49.0	81.7	3.2	3.2	20.0	55.7	65.2	◎
実施例 10	反応物 4	0.15	50.0	60.0	56.0	47.0	78.3	2.9	3.1	20.2	53.9	65.6	○
実施例 11	反応物 5	0.13	49.0	61.0	55.0	50.0	82.0	3.1	3.0	19.8	54.0	63.8	◎
実施例 12	反応物 6	0.15	50.0	59.0	54.0	46.0	78.0	2.9	3.1	21.1	58.2	65.1	◎
比較例 11	反応物 7	0.19	49.0	60.0	48.0	40.0	66.7	3.0	3.3	20.0	40.2	65.2	○
比較例 12	反応物 8	0.20	50.0	60.0	51.0	42.0	70.0	3.1	3.0	19.9	53.0	63.8	○
比較例 13	反応物 9	3.00	50.0	46.0	30.0	28.0	60.9	3.0	3.8	18.9	50.6	60.2	○
比較例 14	反応物 10	3.00	51.0	43.0	30.0	29.0	67.4	2.9	3.9	19.1	52.3	62.5	○
比較例 15	反応物 11	3.00	50.0	40.0	31.0	30.0	75.0	3.0	4.0	19.8	53.1	61.4	○
比較例 16	メルフロー 40	0.25	50.0	61.0	45.0	28.0	45.9	3.0	3.1	19.3	53.1	64.6	○
比較例 17	マイティー	0.28	51.0	61.0	43.0	36.0	59.0	3.1	4.8	16.7	53.7	63.0	△
比較例 18	チューポール HP-8	0.16	50.0	60.0	53.0	40.0	66.7	3.0	5.0	16.8	52.8	64.2	△

[0055]

[Effect of the Invention] As compared with the existing cement water-reducing agent, the cement admixture obtained by this invention shows a high convection effect with a low addition, and has the property that the survival rate of a flow is high and reinforcement will be excellent for one day so that clearly from an example and the example of a comparison. That is, it has a high initial fluidity and the outstanding slump holdout, without bringing about hardening delay to cement constituents, such as mortar and concrete. Furthermore, it excels also in segregation resistance. Furthermore, it is used as a plasticizer, and when it back-\*\*, a high convection effect is shown especially. So, when the cement admixture obtained by the invention in this application is used for engineering works, construction-related construction, etc., workability can be improved remarkably. Moreover, when it uses for casts, such as a box culvert, the concrete secondary product of front-face nature which is remarkably excellent can be obtained.

[Translation done.]